(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 519 616 A1

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 92305055.3

(22) Date of filing: 02.06.92

(51) Int. Cl.5: C08K 3/00, C08K 5/00, C08L 51/06

(30) Priority: 19.06.91 US 717369

(43) Date of publication of application: 23.12.92 Bulletin 92/52

(84) Designated Contracting States: BE DE DK FR GB IT NL SE

(71) Applicant: CHEVRON RESEARCH AND TECHNOLOGY COMPANY
555 Market Street
San Francisco, California 94105(US)

(72) Inventor: Bacskai, Robert
254 Stanford Avenue
Kensington, California 94708(US)
Inventor: Ching, Ta Yen
10 Santa Yorma Court
Novato, California 94945(US)

(74) Representative: Nash, David Allan et al
Haseltine Lake & Co. Hazlitt House, 28
Southampton Buildings, Chancery Lane
London WC2A 1AT(GB)

(54) Oxygen scavenging homogeneous modified polyolefin-oxidizable polymer-metal salt blends.

(57) The invention provides a composition of matter having oxygen scavenger capabilities. The composition comprises a blend of a first polymeric component comprising a polyolefin, the first polymeric component having been grafted with an unsaturated carboxylic anhydride or an unsaturated carboxylic acid, or combinations thereof, or with an epoxide; a second polymeric component having OH, SH or NHR^2 groups where R^2 is H, C_1-C_3 alkyl, substituted C_1-C_3 alkyl; and a metal salt capable of catalyzing the reaction between oxygen and the second polymeric component, the polyolefin being present in an amount sufficient so that the blend is non phase-separated. In the preferred composition maleic anhydride is the grafted material, the second polymeric component is MXD6 nylon and the metal is cobalt. A method of providing a homogeneous blend of a polyolefin with a second polymeric component having OH, SH or NHR^2 groups is also set forth. Articles such as containers for foods and beverages utilizing such compositions and/or such method are provided.

I believe that this is the main reason why such blends are relatively poor oxygen scavengers when compared to PET-MXD6-cobalt salt blends.

The present invention is directed to overcoming the problem as set forth above.

Disclosure Of Invention

Utilizing modified polyolefins, which can be prepared, for example, by grafting a compound such as maleic anhydride or the like, acrylic acid, methacrylic acid, fumaric acid, maleic acid or an epoxide containing compound, onto the polyolefin, in place of all or a portion of the unmodified polyolefin, one can obtain homogenous non phase-separated blends with polyamides such as MXD6. Thereby, the metal salt can be homogeneously dispersed throughout the resulting blend leading to improved oxygen scavenging capability. It should be noted that it is not necessary that all of the polyolefin be modified. Thus, the use of even a relatively small amount of modified polyolefin, along with a relatively major amount of unmodified polyolefin, leads to the formation of a homogeneous non phase-separated blend. If polyolefin alone, unmixed with or instead of such a grafted polyolefin, is used, rather than at least an effective amount of such a grafted polyolefin, blending with MXD6 produces an inhomogeneous phase-separated blend. The blend of the invention has superior oxygen scavenging activity to that made using only unmodified polyolefins. The present invention thus allows the use of what are basically inexpensive polyolefins to produce containers and the like which have good oxygen scavenger capabilities. Note also that copolymers of olefins with other unsaturated monomers are also usable in accordance with the present invention and that the term "polyolefin" is, at times, used herein to include such copolymers.

In accordance with one embodiment of the present invention a composition of matter is provided which has oxygen scavenger capabilities. The composition of matter comprises a blend of

a) a first polymeric component comprising a polyolefin or a copolymer of an olefin and one or more other unsaturated monomers, the first polymeric component having been grafted with an unsaturated carboxylic anhydride or an unsaturated carboxylic acid such as acrylic acid, methacrylic acid, fumaric acid or maleic acid, alone or in combination, or with an epoxide;

b) a second polymeric component having OH, SH or NHR^2 groups where R^2 is H, C_1-C_3 alkyl or substituted C_1-C_3 alkyl; and

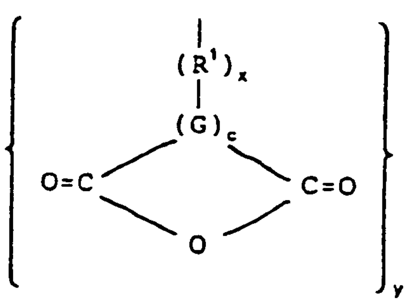
c) a metal salt, the first polyolefin being present in an amount sufficient so that the blend is non phase-separated.

In accordance with another embodiment of the invention a composition of matter having oxygen scavenger capabilities comprises a blend of

a) a first polymeric component comprising a first polyolefin or the first polyolefin along with a second polyolefin, the first polyolefin being representable by the formula:

$$\left\{ -(\underset{\displaystyle J}{\underset{|}{C}}RCR_2)_n- \right\}_a$$

wherein J is either



or

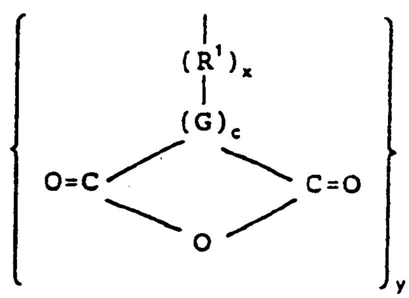
where D = OH, SH or NHR^2, D can be on a side chain or can be a chain terminating group of the polymer and more than one type of D can be attached to the polymer backbone and where R^2 is H, C_1-C_3 alkyl or substituted C_1-C_3 alkyl; and

c) a metal salt, the first polyolefin being present in an amount sufficient so that the blend is non phase-separated.

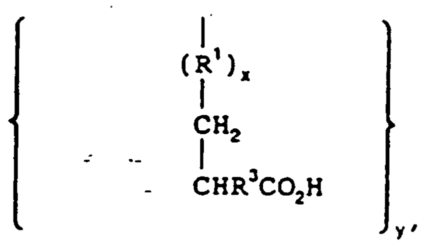
In accordance with still another embodiment of the invention a method is provided of preparing a homogeneous non phase-separated blend of a polyolefin with a polymer having OH, SH or NHR^2 functionality. The method comprises blending the polyolefin with the polymer and with a modified polyolefin representable by the formula:

$$\left\{ -(\underset{\displaystyle J}{\underset{|}{C}}RCR_2)_n- \right\}$$

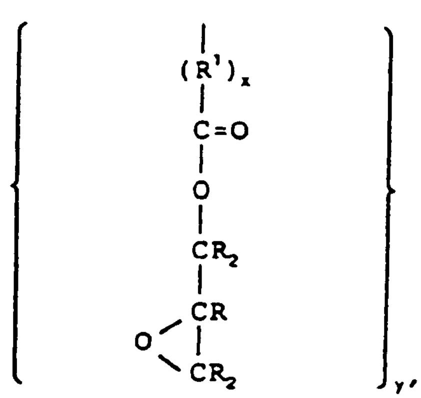
wherein J is either

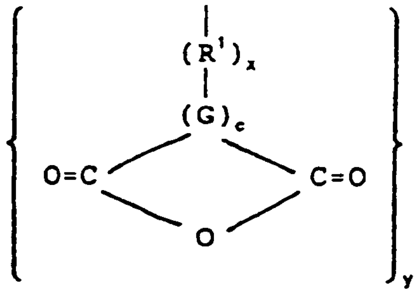


or

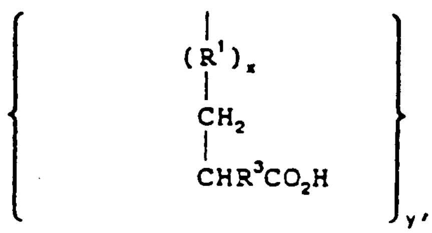


alone or in combination, or

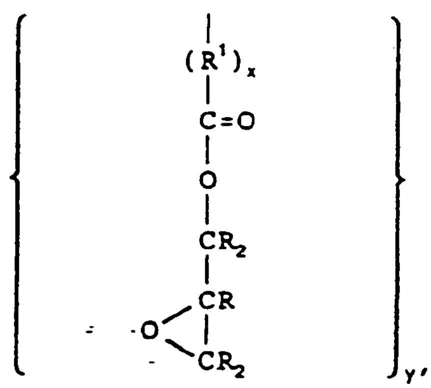




or



alone or in combination, or



wherein $-(CRCR_2)_n-$ represents the polymer backbone with

n = the degree of polymerization,

G represents an organic or substituted organic chain having c carbon atoms bridging between the two C=O groups with c = 2 or 3,

independently each R = hydrogen, a C_1-C_4 alkyl, a substituted C_1-C_4 alkyl, or an ester linkage having 2 to 4 carbon atoms,

R^1 = an organic side chain, including but not limited to repeating polymeric units,

R^3 = H or CH_3

x = 0 or 1 wherein 0 indicates the absence and 1 the presence of the subscripted constituent, and

y = the fraction of substituted monomer units, and the second polyolefin which is represented by the formula:

$$\left\{ -(CR_2CR_2)_m- \right\}_p$$

oxygen, sulfur or nitrogen. Thus, the hydrogen may be part of a hydroxyl group, an amine group or a thio group. In general, the second polymeric component can be represented by the formula:

$$\begin{array}{c} \texttt{-(polymer backbone)-} \\ | \\ D \end{array}$$

where D = OH, SH or NHR^2, D can be on a side chain or can be a chain terminating group of the polymer and more than one type of D can be attached to the polymer backbone and R^2 is H, C_1-C_3 alkyl or substituted C_1-C_3 alkyl. Thus, the second polymeric component can be a polyol, a polythiol, a polyamide, or the like.

The preferred second polymeric component will comprise a polyamide or copolyamide, the latter being a copolymer of polyamides and other polymers. The polymers can be aromatic or aliphatic. The preferred group of polyamides are the MX nylons, with very good results being attainable with MXD6 nylon. These polyamides contain at least 70 mol percent of structural units obtained from m-xylylenediamine alone or a xylylenediamine mixture containing m-xylylenediamine and p-xylylenediamine and an α, ω aliphatic dicarboxylic acid having 6 to 10 carbon atoms. Such polymers have the ability to coordinate to the metal ions of the metal salt thus, it is believed, promoting their own catalytic oxidation.

Examples of polymers as discussed above include the homopolymers such as poly-m-xylylene adipamide and poly-m-xylylene sebacamide, copolymers such as m-xylylene/p-xylylene adipamide copolymers, m-xylylene/p-xylylene pyperamide copolymer and m-xylylene/p-xylylene azelamide copolymers, and copolymers of these homopolymers or copolymer components and aliphatic diamines such as hexamethylenediamine, cyclic diamines such as piperazine, aromatic diamines such as p-bis(2-aminoethyl)benzene, aromatic dicarboxcylic acids such as terephthalic acid, lactams such as ϵ-caprolactam, ω-aminocarboxylic acids such as ω-aminoheptoic acid and aromatic aminocarboxylic acids such a p-aminobenzoic acid.

The MX nylons may have incorporated polymers such as nylon 6, nylon 66, nylon 610 and nylon 11. One preferred aromatic polyamide is the polymer formed by the polymerization of m-xylylene-diamine H_2NCH_2-m-C_6H_4-CH_2NH_2 and adipic acid $HO_2C(CH_2)_4CO_2H$, for example a product manufactured and sold by Mitsubishi Gas Chemicals, Japan, under the designation MXD6. A preferred polyamide of an aliphatic nature is nylon 6.6. The choice of polymers is not critical so long as there are groups and/or atoms in the polymer which have the capacity to contribute to the formation of a complex with the metal.

The formation of polyolefins which have compounds such as maleic anhydride, acrylic acid, methacrylic acid, fumaric acid, maleic acid or epoxy compounds grafted to them is known as are blends of at least some of such compounds with polyamides. Such blends are useful as adhesives and/or as high impact strength molding compounds. Furthermore, such blends may have fillers and reinforcing substances, processing auxiliaries, nucleating agents, pigments and stabilizers, including, inter alia, chalk, quartz, wollastonite, microvite, talcum, calcium stearate, titanium dioxide, carbon black, cadmium sulfide and sterically hindered phenols added to them prior to molding and/or prior to use as adhesives. Such compositions do not, however, act as oxygen scavengers and do not include metal compounds which would catalyze oxidation of the polyamide portion of the blend. Relevant discussions of such blends may be found in, for example, U.S. Patent 4,362,846 of Korber, et al., issued December 7, 1982 and in Canadian patent application 2,003,390 of Abe, et al., all of which are incorporated herein by reference.

In accordance with the invention, the catalytic metal of the metal compound forming the active component in the composition is selected from the group consisting of iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, manganese and zinc. In accordance with a more preferred embodiment of the invention the metal comprises iron, cobalt or nickel, more preferably still, cobalt.

The metal salt may have substantially any anion which does not provide incompatibility problems with the other components or with any food or beverage with which it may be used. Thus, either inorganic or organic anions can be utilized. The metal salt should be relatively uniformly dispersible in the polymeric components. Hence, metal salts wherein the anion is organic are preferred. Good results have been obtained utilizing octoate as the anion but the octoate was chosen primarily for convenience. Other useful anions include, among many others, 2-ethylhexanoate, naphthenate, dodecanate and hexadecanoate.

The composition of the invention may be prepared in any form, for example as particles or granules.

The amount of the metal present in the polymer composition in accordance with the present invention is

Example 2

Compositions Of The Invention

Maleic anhydride (MAH) grafted polyolefins were prepared by reacting HDPE Grade 9122, 1 weight percent MAH and 0.1 weight percent 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane in a twin screw extruder at 180°C. The resulting product had a melt index of 2.2g/10 minutes. The amount of MAH grAfted by this procedure was 0.63 weight percent. The rest of the MAH was evaporated during the reaction. These were then melt mixed in the same twin-screw extruder and under the same conditions as in Example 1 with MXD6, and in some instances cobalt octoate, as well, to produce the compositions listed in Table 2. These compositions were examined by scanning electron microscopy.

Table 2

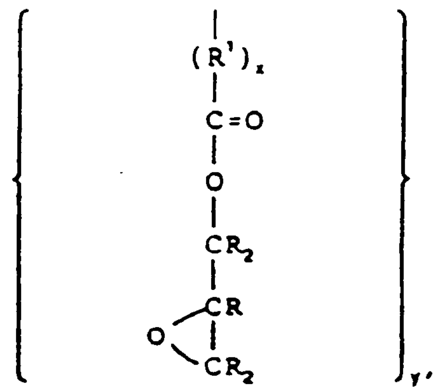
Blend	SEM Results
80% HOPE 15% MAH Grafted HDPE 5% MXD6 200 ppm Co	A continuous phase
65% HDPE 30% MAH Grafted HDPE 5% MXD6 200 ppm Co	A continuous phase
95% MAH Grafted HDPE 5% MXD6 200 ppm Co	A continuous phase
20% MAH Grafted HDPE 80% MXD6	A continuous phase (Fig. 1B)
50% MAH Grafted HDPE 50% MXD6	A continuous phase (Fig. 2B)
80% MAH Grafted HDPE 20% MXD6	A continuous phase (Fig. 3B)

As will be seen by examination of Table 2 and of Figures 1B, 2B and 3B, scanning electron microscopy showed that a homogenous blend was obtained of the maleic anhydride grafted polyolefins with the MXD6 and of the maleic anhydride grafted polyolefins with the MXD6 and the cobalt octoate. This is in contrast to the results set forth in Example 1 and illustrated in Figures 1A, 2A and 3A wherein the polyolefins were not grafted with maleic anhydride. As a result, better oxygen scavenging is attainable using the compositions of the present invention as compared with the prior art compositions.

Industrial Applicability

The present invention provides a composition useful for making articles of manufacture with excellent oxygen scavenging characteristics from inexpensive and readily available polyolefins and provides such articles of manufacture. The articles of manufacture, which can be used as food or beverage containers, exhibit particularly good oxygen scavenging capabilities and are not phase-separated when blended with polyamide type polymers and a metal salt.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification, and this application is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice in the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth, and as fall within the scope of the invention and the limits of the appended claims.



wherein $-(CRCR_2)_n-$ represents the polymer backbone with

n = the degree of polymerization,

G represents an organic or substituted organic chain having c carbon atoms bridging between the two C=O groups with c = 2 or 3,

independently each R = hydrogen, a C_1-C_4 alkyl, a substituted C_1-C_4 alkyl, or an ester linkage having 2 to 4 carbon atoms,

R^1 = an organic side chain, including but not limited to repeating polymeric units,

R^3 = H or CH_3

x = 0 or 1 wherein 0 indicates the absence and 1 the presence of the subscripted constituent, and

y = the fraction of substituted monomer units, and the second polyolefin being represented by the formula:

$$\left\{ -(CR_2CR_2)_m- \right\}_b$$

wherein $-(CR_2CR_2)_m-$ represents the polymer backbone with

m = the degree of polymerization,

a and b represent the weight fractions of the first and second polyolefins in the first polymeric component with

a = 0.005 to 1, and b = 0.995 to 0 .

4. A composition according to any preceding claim, wherein the second polymeric component comprises a polymer representable by the formula:

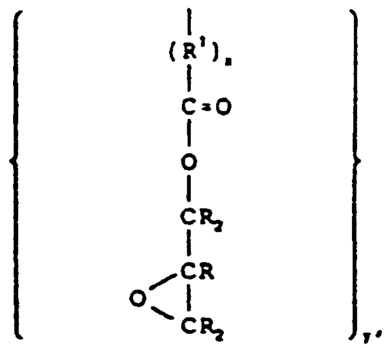
$$-(\text{polymer }\underset{\substack{|\\ D}}{\text{backbone}})-$$

where D = OH, SH or NHR^2 and more than one D can be attached to a polymer backbone and where R^2 is H, C_1-C_3 alkyl or substituted C_1-C_3 alkyl.

5. A composition according to any one of claims 3 or 4, wherein the polymeric backbone

$$(\text{i.e. } -(\underset{|}{C}RCR_2)-)$$

of the first polymeric component comprises polyethylene, polypropylene, polybutylene or copolymers thereof, or an ethylene copolymer with one or more of vinylacetate, methyl, ethyl or butylacrylate, or mixtures of two or more thereof.



wherein $-(CRCR_2)_n-$ represents the polymer backbone with

n = the degree of polymerization,

G represents an organic or substituted organic chain having c carbon atoms bridging between the two C=O groups with c = 2 or 3,

independently each R = hydrogen, a C_1-C_4 alkyl, a substituted C_1-C_4 alkyl, or an ester linkage having 2 to 4 carbon atoms,

R^1 = an organic side chain including but not limited to repeating polymeric units,

R^3 = H or CH_3

x = 0 or 1 wherein 0 indicates the absence and 1 the presence of the subscripted constituent, and

y = the fraction of substituted monomer units, in an amount sufficient to assure production of the homogeneous non phase-separated blend.

14. A blend produced according to the method of claim 13.

15. An article of manufacture produced by moulding the blend according to claim 14 into a desired shape.